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# ANIONIC COPOLYMERIZATION OF METHYL AND CYCLOHEXYL METHACRYLATES

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**Abstract**—The copolymerization of methyl methacrylate (*a*) and cyclohexyl methacrylate (*b*) was studied at room temperature using sodium naphthalene as initiator and dioxane as diluent. The monomer reactivity ratios ($r_a$ and $r_b$), found by a tracer method, are 1·4 ± 0·1 and 0·8 ± 0·1 respectively. Copolymerizations were performed also using alkali metals as initiators and using various diluents; wide variations were found in the apparent monomer reactivity ratios.

Studies of copolymerizations of methyl methacrylate (MMA) with other esters of methacrylic acid initiated radically(1) and by metallic sodium(2) have been reported. Attention was drawn(2) to close similarities between the two sets of results when the comonomer was ethyl, phenyl or benzyl methacrylate and to substantial differences when the comonomer was cyclohexyl methacrylate (CMA); the monomer reactivity ratios for that system in radical reactions at 60° were 0·86 and 1·15 whereas those for reactions at 30° initiated by sodium were 1·96 and 0·49. Further study is now reported for the copolymerization of MMA with CMA using sodium naphthalene or alkali metals for initiation.

## EXPERIMENTAL

The procedures for copolymerizations initiated by metallic initiators have been described already.(2) Homogeneous copolymerizations involving MMA, CMA and sodium naphthalene were performed under rigorous conditions in high vacuum apparatus. All preliminary operations were carried out in interconnected glass vessels attached to the vacuum line.

Sodium naphthalene was prepared by stirring a solution of naphthalene in dioxane (purified by distillation from disodium benzophenone) over a sodium mirror freshly prepared from sodium azide; a slight excess of azide over naphthalene was used. The resulting solution was forced by pressure of pure argon through a glass sinter to remove excess metal and other solids.

The monomers were degassed and then dried by repeated flash distillations on to sodium mirrors. The required volumes of monomers were then distilled into a vessel containing a glass-covered stirrer operated magnetically. The required volume of the solution of sodium naphthalene was forced rapidly by pressure of argon into the vigorously stirred mixture of monomers. The gas was also used to force samples from the reaction mixture at various conversions up to 20 per cent.

Copolymers were recovered by precipitation in cold methanol. $^{14}$C-MMA was used so that compositions of copolymers could be determined by comparison of their specific activities with that of the labelled monomer.(1, 2) Results were treated by the method of Fineman and Ross.(3)

## RESULTS AND DISCUSSION

Table 1 shows typical results for copolymerizations initiated by sodium naphthalene in dioxane at room temperature. The rates of copolymerizations decreased with time and initial rates were not completely reproducible. The results quoted in Table 1 refer to conversions between 5 and 10 per cent but no significant variation of copolymer composition with conversion was found over the range 2–20 per cent. From

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TABLE 1. COPOLYMERIZATIONS OF METHYL AND CYCLOHEXYL METHACRYLATE INITIATED BY SODIUM NAPHTHALENE IN DIOXANE

| Concentrations (mole/l) | | | Mole fraction MMA in feed | Specific activity of copolymer† ($\mu$c/g of carbon) | Mole fraction MMA in copolymer |
|---|---|---|---|---|---|
| Sodium naphthalene* | MMA | CMA | | | |
| <0·005 | 0·557 | 0·074 | 0·883 | 0·198 | 0·911 |
| <0·005 | 0·629 | 0·166 | 0·791 | 0·171 | 0·839 |
| <0·008 | 0·465 | 0·182 | 0·719 | 0·152 | 0·782 |
| <0·005 | 0·442 | 0·268 | 0·623 | 0·125 | 0·689 |
| <0·005 | 0·338 | 0·308 | 0·523 | 0·100 | 0·595 |

* Determined by alkalimetry.

† Specific activity of monomeric $^{14}$C-MMA = 0·237 $\mu$c/g of carbon.

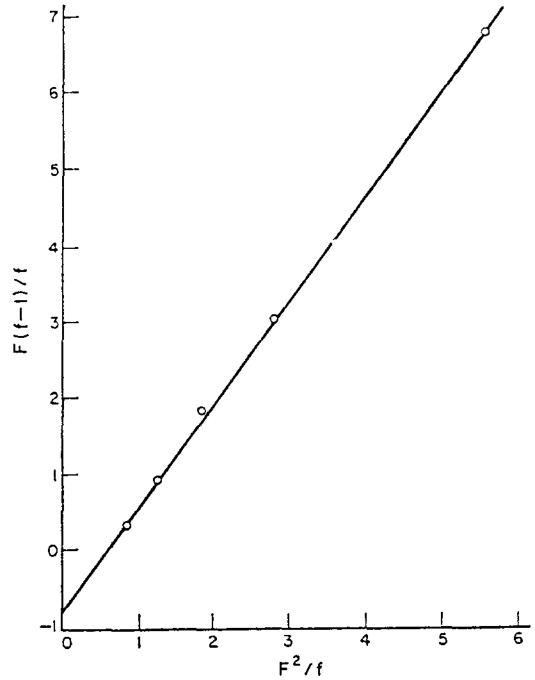

FIG. 1. Fineman–Ross plot for copolymerization at room temperature of methyl and cyclohexyl methacrylates. Diluent is dioxane, initiator is sodium naphthalene.

Fig. 1 and by application of a new procedure$^{(4)}$ for treating data from copolymerizations, it is deduced that

$$r_a = 1\cdot4 \pm 0\cdot1 \text{ (95 per cent probability level)}$$
$$r_b = 0\cdot8 \pm 0\cdot1 \text{ (95 per cent probability level)}$$

so that $1/r_a = 0\cdot71$ and $r_a . r_b = 1\cdot12$.

The decrease of rate with conversion is consistent with rapid initiation and with termination during copolymerization; the latter process might involve impurities, so leading to some irreproducibility, and it might involve attack of growing centres on the ester groups of molecules of monomers. The existence of termination processes seems not to affect the consistency of the results for compositions of copolymers. The copolymerizations can properly be regarded as homogeneous anionic processes. The product $r_a . r_b$ is close to 1 so that the system shows ideal behaviour in that the relative reactivities of the monomers are the same towards the two types of growing centres. O'Driscoll(5) has shown that such behaviour can be expected for the anionic copolymerizations of monomers of similar polarities.

CMA is less reactive than MMA towards the poly MMA anion ($1/r_a = 0{\cdot}71$), but it is slightly more reactive than MMA towards the poly MMA radical ($1/r_a = 1{\cdot}17$). A similar effect occurs for *n*-butyl methacrylate which is more reactive than MMA towards the poly MMA radical ($1/r_a = 1{\cdot}26$)(5) but is less reactive than MMA in copolymerizations initiated by *n*-butyl lithium in toluene.(6) This inversion in the relative reactivities of MMA and CMA cannot be interpreted in terms of polar effects; their polarities, as indicated by "e" or "α" values, are similar.(1) The fact that $r_a > 1$ and $r_b < 1$ shows that monomeric CMA is less reactive than MMA towards both the poly MMA anion and the poly CMA anion. Several factors may contribute towards the lower reactivity of CMA in anionic polymerizations. Solvation of the transition state complex in the anionic growth reaction, leading to significant decrease in activation energy, may be much more effective for MMA than for CMA because of the smaller steric requirements of the methyl group. Further, the cyclohexyl group may destabilize the anionic transition state complex so leading to CMA being less reactive than MMA. It is necessary also to note that the polymer anions and the sodium ions are likely to form contact ion pairs in dioxane so that addition of a molecule of monomer to the polymer anion may be subject to more stringent steric conditions than the addition of monomer to a radical.

The results in Table 2 refer to initiation by alkali metals; wide variations are apparent and systematic trends cannot be detected. Most of the results differ substantially from those corresponding to initiation by sodium naphthalene and some of them correspond to values of $r_a . r_b$ considerably greater than 1. It is considered that, at present, no precise significance can be attached to these results and that it is possible

TABLE 2. COPOLYMERIZATIONS OF METHYL METHACRYLATE (*a*) WITH CYCLOHEXYL METHACRYLATE AT 30°

| Diluent (60% by volume) | Initiator | Monomer reactivity ratios $r_a$ | $r_b$ | $r_a . r_b$ |
|---|---|---|---|---|
| Benzene | Lithium | 1·34 | 1·84 | 2·47 |
| Benzene | Sodium | 1·96 | 0·49 | 0·96 |
| Benzene | Potassium | 2·19 | 0·73 | 1·60 |
| Dioxane | Lithium | 1·57 | 1·27 | 1·99 |
| Dioxane | Sodium | 2·09 | 0·82 | 1·71 |
| Dioxane | Potassium | 1·90 | 0·55 | 1·05 |
| Tetrahydrofuran | Lithium | 1·27 | 0·84 | 1·07 |
| Tetrahydrofuran | Sodium | 1·49 | 0·85 | 1·27 |
| Tetrahydrofuran | Potassium | 2·02 | 0·86 | 1·74 |

only to speculate on the reasons for the apparent anomalies. The heterogeneous nature of the systems is clearly a likely cause of complications. In the early stages of the copolymerizations, the colour associated with the active centres was confined to the immediate vicinity of the catalytic surface but later the colour permeated the whole system and its intensity increased steadily.

The relative concentrations of the comonomers at the surface may well differ from those in the body of the solution and it seems quite possible that copolymerization occurring in the immediate vicinity of the metallic surface should have characteristics quite different from those of copolymerization occurring in a homogeneous system. If this is so, the recovered copolymers can be regarded as mixtures of two types of material, one being a copolymer formed at or close to the metallic surface and the other being a copolymer formed in the bulk of the reaction mixture after the growing centre has detached itself from the surface. Both types of structure would be expected in most of the recovered molecules of copolymer. It is significant that scatter of results was pronounced in some of these systems as indicated by data in Table 3 which refers to copolymerizations involving equal initial molar concentrations of monomer in dioxane. The scatter can be attributed in part at least to uncontrolled variations in the experimental conditions leading to differences between the proportions of the two types of material in the recovered copolymers. From the monomer reactivity ratios already quoted for initiation by sodium naphthalene, the calculated value of (MMA)/CMA) in the copolymer is 1·35. The large variations of monomer reactivity ratios with the natures of the alkali metal and the diluent are not confined to the system MMA–CMA. Similar effects were found for the copolymerizations of MMA with ethyl and phenyl methacrylates.

TABLE 3. COMPOSITIONS OF COPOLYMERS ISOLATED AT VARIOUS CONVERSIONS OF EQUIMOLAR MIXTURES OF METHYL AND CYCLOHEXYL METHACRYLATES IN DIOXANE

| Initiator | % conversions | (MMA)/CMA) in copolymers |
|---|---|---|
| Lithium | 9·5, 11·3, 16·4 | 1·27, 1·22, 0·96 |
| Sodium | 4·8, 18·8, 33·3 | 1·60, 1·44, 1·87 |
| Potassium | 11·7, 16·0, 28·9 | 1·94, 1·95, 1·92 |

It must be concluded that the results found for copolymerizations initiated by alkali metals have limited significance. Even if the same alkali metal and the same diluent are used for a set of monomers, the results should not be used for purposes such as the comparison of the reactivities of monomers towards reference anions.

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**Résumé**—On a étudié la copolymérisation du méthacrylate de méthyle (*a*) et le méthacrylate de cyclohexyle (*b*) à la température ambiante en utilisant le naphtalène sodium comme amorceur et le dioxane comme diluant. Les rapports de réactivité des monomères ($r_a$ et $r_b$), déterminés par la méthode des traceurs, valent 1,4 ± 0,1 et 0,8 ± 0,1 respectivement.

Des copolymérisations ont également été réalisées en utilisant des métaux alcalins comme amorceurs et divers diluants; on a trouvé d'importantes variations dans les rapports de réactivité apparents du monomère.

**Sommario**—La copolimerizzazione del metilmetacrilato (*a*) e del cicloesilmetacrilato (*b*) é stata studiata a temperatura ambiente usando sodio naftalina come iniziatore e diossano come diluente. I rapporti di reattività dei monomeri ($r_a$ e $r_b$), trovati mediante uso di traccianti, sono 1,4 ± 0,1 e 0,8 ± 0,1 rispettivamente. Le copolimerizzazioni furono eseguite anche usando metalli alcalini come iniziatori e usando vari diluenti; sono state trovate ampie variazioni negli apparenti rapporti di reattività dei monomeri.

**Zusammenfassung**—Die Copolymerisation von Methylmethacrylat (*a*) und Cyclohexyl-methacrylat (*b*) wurde bei Zimmertemperatur untersucht unter Verwendung von Natriumnaphthalin als Initiator und Dioxan als Verdünnungsmittel. Die durch radioaktive Markierung gemessenen Verhältnisse der Monomerreaktivitäten ($r_a$ und $r_b$) sind 1·4 ± 0·1 und 0·8 ± 0·1 jeweils.

Copolymerisationen wurden auch unter Verwendung von Natriummetallen als Initiatoren und mit verschiedenen Verdünnungsmitteln durchgeführt. Es wurden erhebliche Unterschiede für die scheinbaren Monomer-Reaktivitätsverhältnisse gefunden.